



A high-powered concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ cathode material for lithium ion batteries



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HIGHLIGHTS

- Concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})(\text{OH})_2$ is prepared via co-precipitation.
- $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ contains 90% core material of $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$.
- $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ has better electrochemical properties than $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$.
- The capacity of $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ is 195 mAh g^{-1} at 1C between 2.8 and 4.3 V.
- The initial capacity retains 95.5% after 100 cycles.

ARTICLE INFO

Article history:

Received 29 January 2014

Received in revised form

24 March 2014

Accepted 11 April 2014

Available online 24 April 2014

Keywords:

Lithium ion batteries

Cathode materials

Concentration-gradient

High capacity

Rate performance

ABSTRACT

A high-powered concentration-gradient cathode material with an average composition of $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ has been successfully synthesized by a co-precipitation method. The $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ has a core of $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ that is rich in Ni and a concentration-gradient shell having decreased Ni content and increased Mn content. The electrochemical properties of the concentration-gradient material are studied and compared to those of the core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ material alone. In the concentration-gradient material of $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$, the Ni-rich core delivers a very high capacity, while the Mn-rich concentration-gradient shell improves the cycling stability and rate performance. The electrochemical properties of this cathode material are found to be far superior than those of the core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ material. At room temperature, the initial capacity of the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ is 195 mAh g^{-1} at 1C between 2.8 and 4.3 V and retains 95.5% after 100 cycles. Moreover, the composite has a good rate performance with a high capacity of about 190 mAh g^{-1} even at 2C rate.

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1. Introduction

The rechargeable lithium-ion battery has become a common power source for portable electronic devices due to its high energy density, high voltage, and long cycle life. Recently, effort has increased on developing lithium-ion batteries for plug-in hybrid vehicles (PHEVs) and electric vehicles (EVs) [1]. However, commercialization of lithium-ion batteries for the automobile industry needs to overcome the low capacity and inadequate thermal stability of current cathode materials. Ni-rich $\text{Li}(\text{Ni}_{1-x}\text{M}_x)\text{O}_2$ (M = transition metal, $x \leq 0.2$) compounds have attracted much interest as cathode materials for PHEVs and EVs because of their

relatively low cost, low toxicity and high reversible capacity [2,3]. However, the Ni-rich materials have also shown poor cycling life due to oxygen release from the highly delithiated $\text{Li}_{1-\delta}(\text{Ni}_{1-x}\text{M}_x)\text{O}_2$ host structure [4,5]. In addition, Ni is oxidized from the 3+ to 4+ state and forms a more stable compounds of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ (NaCl structure) during cycling, which increases the interfacial impedance and thus decreases the cycle life of the cell [6,7].

One approach to improve the electrochemical properties of Ni-rich materials is to coat the cathode with a thin layer of metal compound. For enhancing the electrochemical stability of Ni-rich $\text{Li}(\text{Ni}_{1-x}\text{M}_x)\text{O}_2$, stable compounds such as AlPO_4 [8], AlF_3 [9,10], SiO_2 [11], MgO [12] and TiO_2 [13] have been used to coat its surface to decrease the electrode/electrolyte interface reactions. These coated materials exhibit positive results with improved electrochemical performance. This improvement is resulted mainly from the stabilization of the charge transfer resistance at the interface

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that caused by the cathode active materials being protected from the generated HF in the electrolyte [7,9,10]. However, these core–shell materials exhibited a sharp composition change on the core–shell interface and a structural mismatch between the core and shell materials, which may lead shell layer to strip from the core material during long repeated cycling. Sun et al. developed a concentration-gradient material that has a bulk core rich in Ni and a stable concentration-gradient layer having gradually reduced Ni concentration and increased Mn concentration [14,15]. $\text{Li}(\text{Ni}_{0.72}\text{Co}_{0.18}\text{Mn}_{0.10})\text{O}_2$ and $\text{Li}(\text{Ni}_{0.83}\text{Co}_{0.07}\text{Mn}_{0.10})\text{O}_2$ are two examples for this kind of concentration-gradient materials which achieved not only high reversible discharge capacity of 188 mAh g^{-1} and 195 mAh g^{-1} respectively (4.3 V cut-off voltage and 0.2C), but also excellent cycle life with capacity retention of 95.3% and 92.1% after 50 cycles. However, these concentration-gradient materials delivered low discharge capacity at high C rate. For example, concentration-gradient $\text{Li}(\text{Ni}_{0.83}\text{Co}_{0.07}\text{Mn}_{0.10})\text{O}_2$ shown a discharge capacity of 172 mAh g^{-1} at 2C.

In this study, we synthesized a cathode material $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ which has a core of $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ and a stable concentration-gradient shell layer. Its structure, morphology and electrochemical performance were investigated. The concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ shows not only high discharge capacity, but also good cyclic stability and rate performance. $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ was also prepared and studied for comparison.

2. Experimental

To obtain core–shell particles with the desired composition, we used spherical $(\text{Ni}_{0.9}\text{Co}_{0.1})(\text{OH})_2$ (Jintian Energy Co. Ltd, China) as the core. The concentration-gradient precursor was designed as $(\text{Ni}_{0.9}\text{Co}_{0.1})_{0.9}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.1}(\text{OH})_2$ and prepared by a co-precipitation method. The core $(\text{Ni}_{0.9}\text{Co}_{0.1})(\text{OH})_2$ was added into a continuously stirring tank reactor (CSTR) which had contained $\text{NH}_3 \cdot \text{H}_2\text{O}$ aqueous as the chelating agent. Stoichiometric $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were mixed and dissolved in DI water to form two mixed metal ions solution of 1.5 mol L^{-1} , a Ni-poor aqueous solution (Ni:Co:Mn = 1:1:1 in molar ratio) and a Ni-rich aqueous solution (Ni:Co = 9:1 in molar ratio). The Ni-poor aqueous solution was continuously pumped into the Ni-rich aqueous solution which was stirred strongly. At the same time, the homogeneously mixed solution was continuously pumped into the CSTR with a N_2 atmosphere. Control the flowing speed to make the two metal ions solutions exhausted simultaneously. A NaOH solution of 3.0 mol L^{-1} and a $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution of 2.0 mol L^{-1} were separately fed into the CSTR. The pH, temperature, and stirring speed of the mixture in the reactor were set to 11.5, 50°C , and 600 rpm, respectively. After reaction finished, the precipitate was aged for 24 h, and then the obtained precipitate was filtered, washed and dried at 80°C in an oven for 24 h. Then the precursor was thoroughly mixed with $\text{LiOH} \cdot \text{H}_2\text{O}$ in a ratio of Li/M = 1.03:1. The mixture was calcined at 550°C for 4 h in the air and then at 750°C for 12 h with an O_2 atmosphere to obtain final materials. Homogeneous $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ material was prepared by directly mixing $(\text{Ni}_{0.9}\text{Co}_{0.1})(\text{OH})_2$ and $\text{LiOH} \cdot \text{H}_2\text{O}$, and the calcined process was same as that for the concentration-gradient material.

The chemical composition of the resulting powders was evaluated by the inductively coupled plasma test (ICP). The crystalline phase of the prepared materials was determined by X-ray diffraction in the 2θ value range from 10° to 80° (D/max-r A type Cu Ka1, 40 kV, 300 mA, Japan). From the XRD data, the lattice parameters were calculated by a least-squares method. The microstructure of powders was observed by scanning electron microscopy equipped with an EDAX energy disperse X-ray spectrometer (SEM, JEOLJSM-

6360LV). Cross-sections of the particles were prepared by embedding the material in an epoxy and then grinding it on metallographic sand papers.

The electrochemical performance of the synthesized materials was examined by using coin type cells (CR2025), which were assembled in a glove box filled with dry argon gas. The cathode was fabricated with a mixture of prepared powder (80 wt%), carbon black (10 wt%), and polyvinylidene fluoride (PVDF) binder (10 wt%) in *N*-Methylpyrrolidone. The obtained slurry was spread onto Al foil and dried in a vacuum oven at 120°C for 12 h. Circular discs with a diameter of 10 mm were punched out as the positive electrode. A typical disk electrode has a weight of 8 mg and a thickness of $80 \mu\text{m}$. The electrolyte solution was 1 mol L^{-1} LiPF_6 in a mixture of EC–DMC–EMC (1:1:1, volume ratio). Celgard 2400 was used as the separator and lithium foil as the negative electrode. Charge and discharge tests were performed on a LAND CT2001A system in the potential range of 2.8–4.3 V (versus Li/Li^+) at 25°C and 55°C . The rate test varied from 0.1C to 2C in the same potential range. Electrochemical impedance spectroscopy (EIS) measurements were performed on cells in the fully discharged state. The amplitude of the a.c. signal was 5 mV over the frequency range of 1 MHz and 10 mHz.

3. Results and discussion

The total average chemical composition of the as-prepared concentration-gradient material was found to be $(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})(\text{OH})_2$, as determined by ICP. Table 1 shows the chemical composition of the precursors and final samples obtained from ICP. The measured compositions of these samples are close to their target compositions. Especially, the ratio of Ni:Co:Mn of the concentration-gradient cathode material is 0.848:0.121:0.031, which is in well agreement with the expected molecular formula $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})_{0.9}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.1}\text{O}_2$.

SEM images of core and concentration-gradient precursors and their corresponding lithiated oxides are showed in Fig. 1. The raw material $(\text{Ni}_{0.9}\text{Co}_{0.1})(\text{OH})_2$ (Fig. 1a) has a nice spherical morphology with smooth surface and a diameter of 3–15 μm . In comparison, the coated concentration-gradient precursors (Fig. 1b) have a rough and fluffy surface with a diameter of 5–17 μm . As expected, the particles of the concentration-gradient $(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})(\text{OH})_2$ precursors were larger than the core $(\text{Ni}_{0.9}\text{Co}_{0.1})(\text{OH})_2$ precursors after coating concentration-gradient shell on the core particles. After lithiation at high temperature, both the core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ (Fig. 1c) and the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ (Fig. 1d) keep the spherical morphology of precursors.

To determine the composition change in the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ oxide, we carried out EDXS on the cross-section of a single particle. The atomic ratio of Ni, Co, and Mn were obtained across the diameter (about 11.2 μm of the particle, as shown in Fig. 2). The core consists of a molar ratio of 0.9 Ni and 0.1 Co, which is consistent with the core sample. The Ni and Co molar ratio were maintained constant through the core, with a thickness of about 9 μm in the middle. In the concentration-gradient shell, molar ratio of Ni decreased gradually, while the Co

Table 1
Chemical composition of the designated and observed samples.

Chemical formula of the designated samples	Main elements ratio of the prepared samples as analyzed
$(\text{Ni}_{0.9}\text{Co}_{0.1})(\text{OH})_2$	Ni:Co = 0.902:0.098
$(\text{Ni}_{0.843}\text{Co}_{0.123}\text{Mn}_{0.033})(\text{OH})_2$	Ni:Co:Mn = 0.846:0.122:0.032
$\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$	Ni:Co = 0.903:0.097
$\text{Li}(\text{Ni}_{0.843}\text{Co}_{0.123}\text{Mn}_{0.033})\text{O}_2$	Ni:Co:Mn = 0.848:0.121:0.031

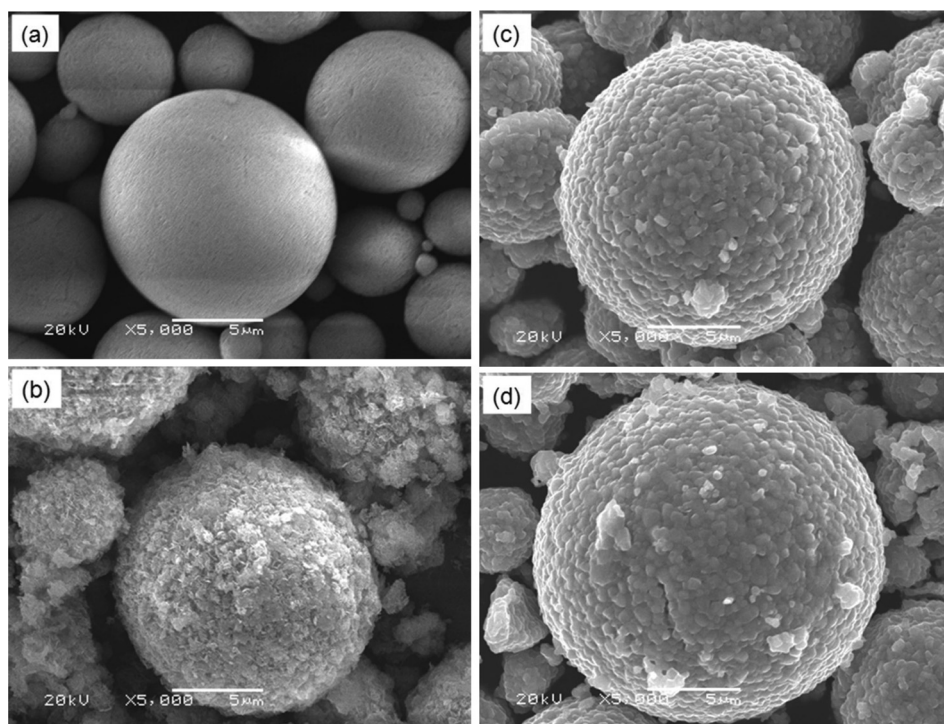


Fig. 1. SEM images of (a) core $(\text{Ni}_{0.9}\text{Co}_{0.1})(\text{OH})_2$, (b) concentration-gradient $(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})(\text{OH})_2$, (c) core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ and (d) concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$.

and Mn molar concentration increased steadily, resulting in a total average composition of $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$. The thickness of the concentration-gradient shell is about $1.3 \mu\text{m}$. The EDXS test shows that the molar ratio of Ni:Co:Mn on the surface of the concentration-gradient precursor particle is about 0.57:0.25:0.18.

Fig. 3a and b shows XRD patterns for the raw material $(\text{Ni}_{0.9}\text{Co}_{0.1})(\text{OH})_2$ and the prepared concentration-gradient precursor $(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})(\text{OH})_2$, which could be indexed well with the typical diffraction peaks of $\text{Ni}(\text{OH})_2$. Fig. 3c and d are XRD patterns for $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ and $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$. Both exhibit a well-defined layer structure based on a hexagonal $\alpha\text{-NaFeO}_2$ structure with a $R\bar{3}m$ space group without any impurity phases. Due to the similarity in their crystal structure, the XRD peaks of the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ overlap those of $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$. But the peak intensity of the concentration-gradient sample is weaker than that of the core sample. It seems that concentration-gradient coating affects slightly the crystalline of $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$.

Lattice parameters of the calcinated powders were calculated from the XRD patterns, and results are given in Table 2. The calculated lattice parameters a , c and V for the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ are a little larger than those for the core material $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$. Recently, Lee et al. showed that $\text{Li}(\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2})\text{O}_2$ has larger lattice parameters a and c than those of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ due to partial formation of Ni^{2+} ($r = 0.69 \text{ \AA}$) from Ni^{3+} ($r = 0.60 \text{ \AA}$) in the structure [16]. Reducing Ni amount but increasing Mn content results in formation of Ni^{2+} and Mn^{4+} . The difference in the ionic radii for the transition metal element consequently affects the resulting lattice parameter. The I_{003}/I_{104} value is commonly used to indicate cation ordering in Ni-rich cathode material for Li-ion batteries depending on the location of lithium and metal ions. The high value of I_{003}/I_{104} means low degree of the cation mixing [17,18], which is one of the main reasons causing Ni-rich cathode material's structure unstability during cycling. Here, The I_{003}/I_{104} value of the concentration-gradient

sample is much higher than that of the core sample, which means a more superior layered structure of the concentration-gradient sample and may help to improve the electrochemical performance [19].

Fig. 4 illustrates the initial charge–discharge curves for $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ and the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ at a current density of 18 mA g^{-1} (0.1C) in 2.8–4.3 V. As seen in Fig. 4, $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ electrode delivers a very high initial discharge capacity of 214.5 mAh g^{-1} , and the concentration-gradient sample $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ shows a slightly lower initial capacity of 209.4 mAh g^{-1} due to the lower Ni content.

Fig. 5a shows the cycle performance of $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ and the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ at 180 mA g^{-1} (1C) and room temperature (25°C) in 2.8–4.3 V range. The initial discharge capacity of the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ is 195.0 mAh g^{-1} , compared to 197.8 mAh g^{-1} for the core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$. However, 95.5% (186.3 mAh g^{-1}) of the initial capacity are retained for the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ after 100 cycles versus only 78.3% (154.8 mAh g^{-1}) for $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$. It seems that the concentration-gradient layer effectively improves the cyclic stability of $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ as cathode material for lithium ion batteries. When the operating temperature increased to 55°C , this kind of electrochemical stability for concentration-gradient sample is more obvious as shown in Fig. 5b. The concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ shows an initial discharge capacity of 216.3 mAh g^{-1} and retains 87.9% (190.1 mAh g^{-1}) after 100 cycles. For comparison, the core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ retains only 62.3% (140.0 mAh g^{-1}) of initial capacity of 227.8 mAh g^{-1} over the same cycling period. The excellent Li^+ intercalation/deintercalation stability of the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ is mainly due to the stable concentration-gradient shell with increasing Mn concentration toward the particle surface. Some studies have shown that the poor cycling performance of Ni-rich materials could originate from the formation of impurity

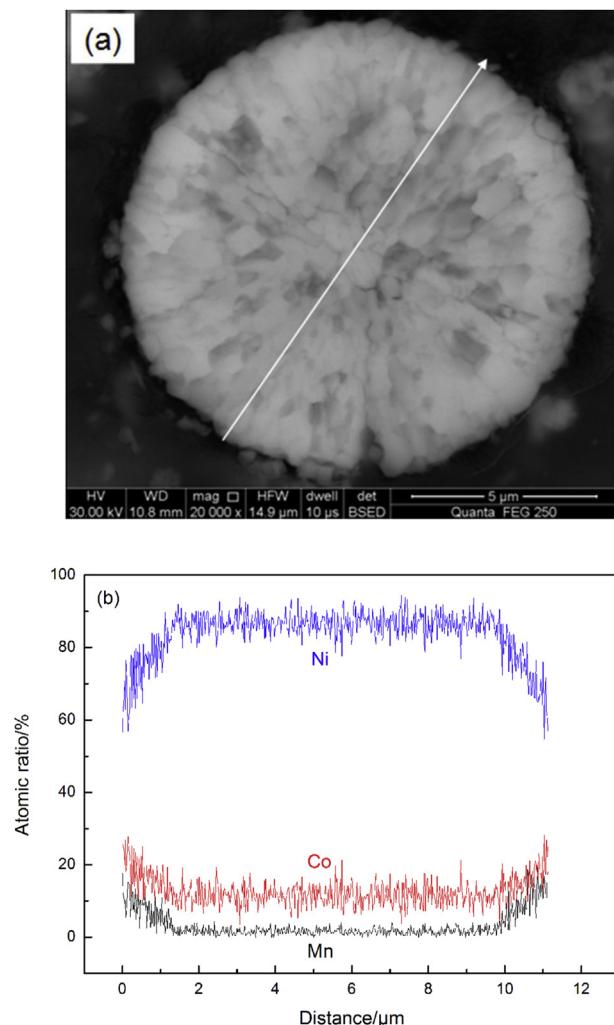


Fig. 2. SEM image of the cross-section (a) and energy disperse X-ray spectrometer (EDXS) image (b) of the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$.

$\text{Li}_x\text{Ni}_{1-x}\text{O}$ phase from $\text{Li}_{1-\delta}(\text{Ni}_{1-x}\text{M}_x)\text{O}_2$ due to the presence of highly reactive and unstable Ni^{4+} , which can increase the interfacial impedance and thus decrease the cycle life of the cell [7,20]. The stable Mn^{4+} and the reduced amount of Ni^{4+} on the particle surface could play important roles in stabilizing the interface between the cathode and the electrolyte by suppressing the increase in interfacial impedance, which enhances the capacity retention [21].

Fig. 6 shows the rate performance of $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ and the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$. The cells were charged and discharged at 0.1C, 0.2C, 0.5C, 1C and 2C rates for continued 5 cycles, respectively. As shown in Fig. 6, the capacity of the concentration-gradient sample at 2C is 190.2 mAh g^{-1} , 90.8% of the value of 209.4 mAh g^{-1} at 0.1C. For the core sample, the two values are 152.1 mAh g^{-1} and 70.9%. It is clear that the concentration-gradient sample displays better rate performance due to the low degree of cation mixing and regular layered hexagonal structure. Li^+ can unhinderedly diffuse in the crystal of the concentration-gradient sample, because of less Ni^{2+} barriers and more ordered passway [22]. Thus, the concentration-gradient shell has a beneficial effect on the rate performance of the core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$.

Electrochemical impedance spectroscopy (EIS) can be used to investigate the kinetic process of lithium intercalation/

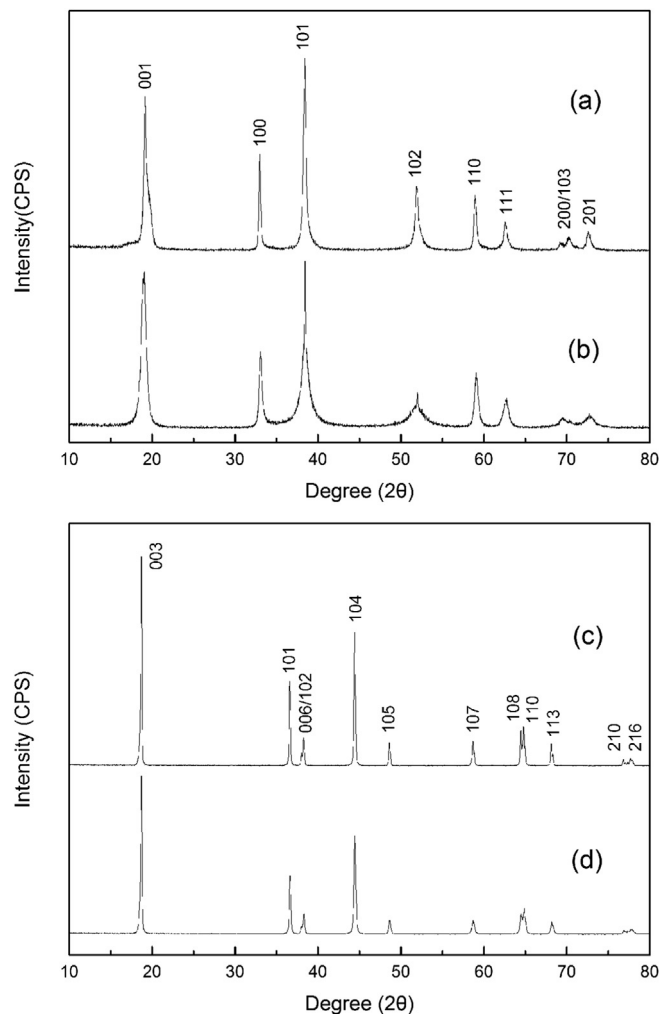


Fig. 3. XRD patterns of (a) core $(\text{Ni}_{0.9}\text{Co}_{0.1})(\text{OH})_2$, (b) concentration-gradient $(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})(\text{OH})_2$, (c) core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$, (d) concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$.

deintercalation into electrodes [23]. EIS experiments were carried out at the charged state of 4.3 V before cycle and after 100 cycles at room temperature (25 $^{\circ}\text{C}$) for the core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ and the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$. The Nyquist plots of cells are presented in Fig. 7. The simplified equivalent circuit model is constructed to analyze the impedance spectra. In this model, R_s represents the bulk resistance and reflects combined resistance of the electrolyte, separator and electrodes, etc.; R_{sf} and CPE1 are assigned to the resistance and film capacitance of Li^+ migration through the surface film which are reflected by the semi-circle at the high frequency region; R_{ct} and CPE2 denotes the charge-transfer resistance and interfacial capacitance between the electrolyte and electrodes which are associated with the second semi-circle appearing at medium frequency region; R_w at low frequency region represents Warburg impedance which is reflected by the inclined line in the lower-frequency range.

Table 2

Lattice parameters of the core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ and the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$.

Molecular formula	$a/\text{\AA}$	$b/\text{\AA}$	Volume/ \AA^3	I_{003}/I_{104}
$\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$	2.8723 (7)	14.1869 (5)	101.37 (2)	1.592
$\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$	2.8746 (9)	14.1882 (7)	101.53 (3)	1.623

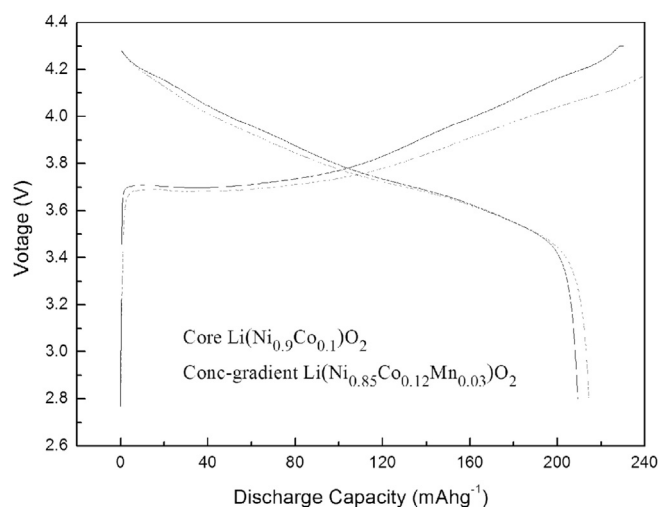


Fig. 4. Initial charge–discharge curves of the core Li(Ni_{0.9}Co_{0.1})O₂ and the concentration-gradient Li(Ni_{0.85}Co_{0.12}Mn_{0.03})O₂ cells at 0.1C in 2.8–4.3 V.

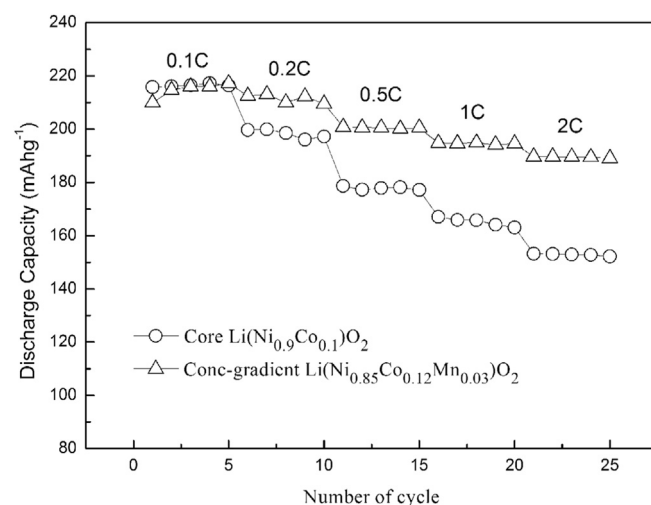


Fig. 6. Rate performance of the core Li(Ni_{0.9}Co_{0.1})O₂ and the concentration-gradient Li(Ni_{0.85}Co_{0.12}Mn_{0.03})O₂ cells at 25 °C.

Chen et al. reported that impedance of lithium ion cells is mainly attributed to cathode impedance, especially charge-transfer resistance R_{ct} [24]. Thus, some information of cathode surface during cycling can be obtained by comparing the second semi-circle after

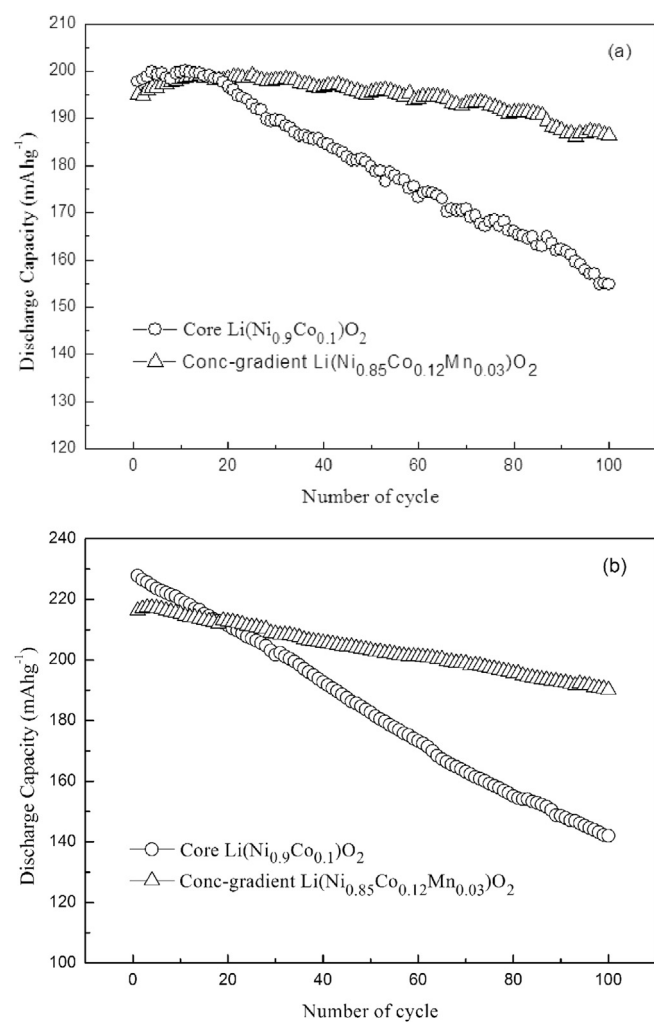


Fig. 5. Cyclic performance of the core Li(Ni_{0.9}Co_{0.1})O₂ and the concentration-gradient Li(Ni_{0.85}Co_{0.12}Mn_{0.03})O₂ cells at 1C in 2.8–4.3 V voltage range at: (a) 25 °C and (b) 55 °C.

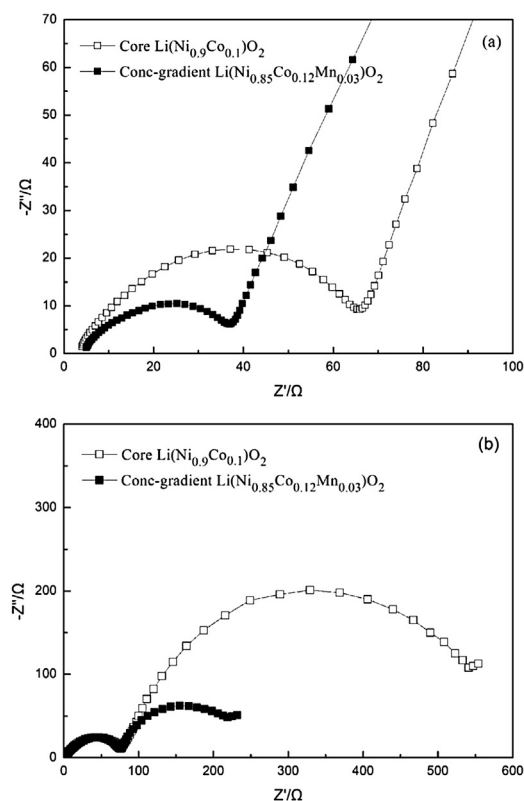
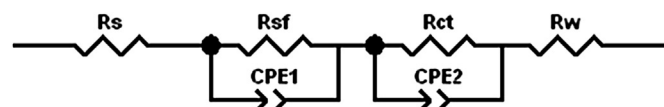


Fig. 7. Equivalent circuit model and Nyquist plots of: (a) core Li(Ni_{0.9}Co_{0.1})O₂ and concentration-gradient Li(Ni_{0.85}Co_{0.12}Mn_{0.03})O₂ samples before cycle, (b) core Li(Ni_{0.9}Co_{0.1})O₂ and Conc-gradient Li(Ni_{0.85}Co_{0.12}Mn_{0.03})O₂ samples after 100 cycles.

Table 3

Charge-transfer resistance (R_{ct}) for the core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ and the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$.

Samples	R_{ct} (Ω)
Core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ (before cycle)	61.8
Conc-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ (before cycle)	31.9
Core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ (after 100 cycles)	460.2
Conc-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ (after 100 cycles)	143.3

cycles, which reflects R_{ct} . Variations in R_{ct} as a function of cycle number for the core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ and concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ electrodes are represented in Table 3. The value of the core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ cells before cycle is only 61.8 Ω but increases rapidly with cycling, and reaches 460.2 Ω after 100 cycles. However, the R_{ct} of the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ increases fairly slowly, growing from 31.9 Ω before cycle to 143.3 Ω after 100 cycles. The stable charge-transfer resistance for the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ electrode mainly results from the stable outer-layer, which has lower Ni content, higher Mn content and weaker Li/Ni mixing. Therefore, the lower charge-transfer resistance of the electrode/electrolyte interface can be used to explain why the concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ has an improved electrochemical performance compared with the core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$.

4. Conclusions

The core–shell type $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ cathode material with concentration-gradient shell layer has been successfully synthesized by a co-precipitation method. Its morphological and electrochemical properties were compared with those of the core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$. The Ni-rich $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ core delivered a high capacity, and the Ni-poor concentration-gradient layer provided improved cycle life. The initial capacity of a concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ electrode cycled to 4.3 V at 55 °C (1C) was 216.3 mAh g^{-1} and retained 87.9% after 100 cycles, whereas the core $\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$ electrode had a capacity retention of only 62.3%. The concentration-gradient $\text{Li}(\text{Ni}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03})\text{O}_2$ also exhibited improved rate capacity compared with the core

$\text{Li}(\text{Ni}_{0.9}\text{Co}_{0.1})\text{O}_2$. This enhanced electrochemical stability is attributed to the increased stable Mn^{4+} content and the reduced Ni^{4+} amount in the particle surface after charging, which results in a significant structural stability. This feature has an evident effect on depressing the increase of charge-transfer resistance over cycling and thus enhances the cycling performance. This Ni-rich concentration-gradient cathode material which shows excellent cyclability and rate capacity has great potential to be used in developing new large-scale power source for the automobile.

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